

Acta Cryst. (1999). **C55**, 1535–1536

Bis(hydrazinium) 4-hydroxy-1-oxo-2*H*-phthalazine-6,7-dicarboxylate

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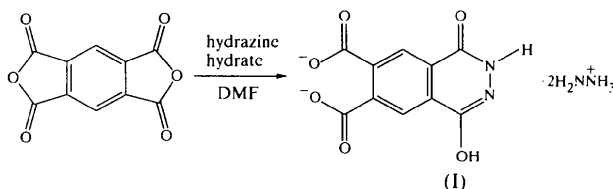
(Received 18 March 1999; accepted 3 June 1999)

Abstract

The structure of the title compound, $2\text{N}_2\text{H}_5^+\cdot\text{C}_{10}\text{H}_4\text{-N}_2\text{O}_6^{2-}$, consists of alternate layers of phthalazine dianions and hydrazinium cations linked by an extensive network of hydrogen bonds. One of the independent cations also forms a close ion pair with a carboxylate group of the anion without a hydrogen bond.

Comment

In our quest to identify relatively inexpensive reagents that possess a recognition site for metal ions and/or a hydrogen-bonding motif, the phthalazine derivative bis(hydrazinium) 4-hydroxy-1-oxo-2*H*-phthalazine-6,7-dicarboxylate, (I), has been prepared. The compound was synthesized in one simple step from the abundant starting material benzene-1,2,4,5-tetracarboxylic anhydride and hydrazine hydrate as outlined below:



Compound (I) is readily soluble in water. The molecular structure of the compound is shown in Fig. 1. Analysis of the ring bond lengths in (I) revealed that the phthalazine moiety exists in the expected more stable tautomeric form (Heine *et al.*, 1980); C4—O2 1.253 (2), C4—N3 1.354 (2), N2—N3 1.381 (2), N2—C1 1.298 (2) and C1—O1 1.336 (2) Å. Other bond lengths and angles are in agreement with a central benzene ring and two appended carboxylate groups. The packing of the molecules in the crystal may be described as alternate layers of cations and anions linked by an extensive network of hydrogen bonds (Fig. 2 and Table 1). The layers are parallel to the *bc* plane. The anion layers are built of stacks (along the *c* direction) of antiparallel phthalazine

moieties; the stacks are linked together in the *b* direction by O1—H···O2(*x*, *y* − 1, *z*) hydrogen bonds. Interplanar distances in a stack are 3.264 (2) and 3.334 (2) Å, the shortest interatomic contacts between neighbouring molecules in a stack being C9···O2(−*x*, 2 − *y*, −*z*) 3.343 (2) Å and C9···C9(−*x*, *y*, $\frac{1}{2}$ − *z*) 3.336 (2) Å. Surprisingly, the shortest interatomic distance [O6···N4S 2.657 (2) Å] between non-H atoms of counter-ions does not correspond to a hydrogen bond but to an electro-

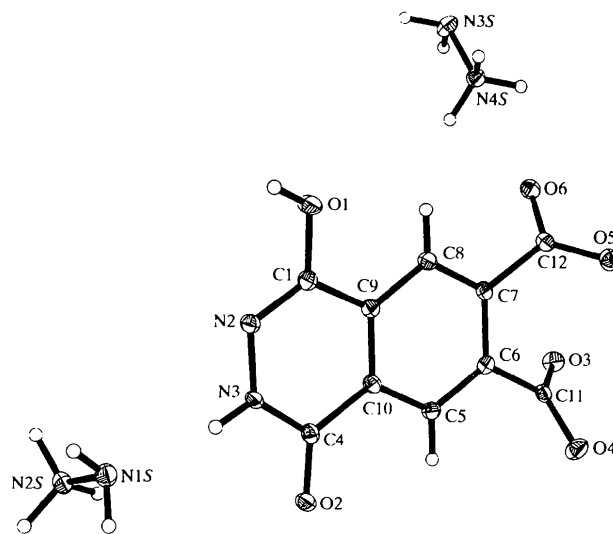


Fig. 1. The molecular structure of (I) and the atom-labelling scheme. Atomic displacement ellipsoids are at the 50% probability level.

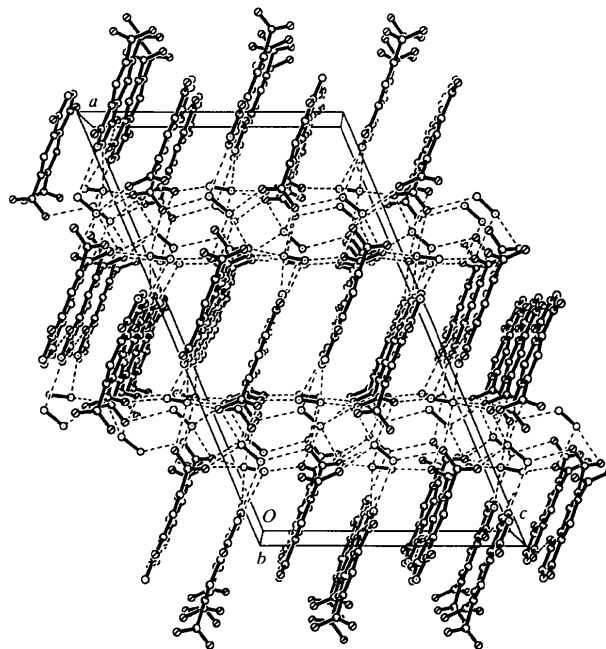


Fig. 2. The crystal packing of (I) viewed along the *b* axis. H atoms have been omitted for clarity.

static interaction. Indeed, all H atoms on the N4S atom are involved in hydrogen bonding with atoms of other anions.

Experimental

Compound (I) was prepared by refluxing benzene-1,2,4,5-tetracarboxylic anhydride (2 g, 11.7 mmol; Aldrich) and hydrazine hydrate (25 equivalents) in dry dimethylformamide (100 ml) for 12 h under nitrogen. The solvent was removed and recrystallization of the crude product from a water-methanol mixture (*ca* 1:4) afforded a yellow solid [¹H NMR (*d*₆-DMSO): δ 6.18 (*s*, 4H), 8.34 (*s*, 6H), 8.83 p.p.m. (*s*, 2H)]. Slow vapour diffusion of methanol into a saturated solution of the compound in water afforded yellow crystals suitable for X-ray crystallography.

Crystal data



$M_r = 314.27$

Monoclinic

$C2/c$

$a = 25.300$ (5) Å

$b = 7.366$ (2) Å

$c = 14.609$ (3) Å

$\beta = 113.62$ (3)°

$V = 2494.4$ (9) Å³

$Z = 8$

$D_x = 1.674$ Mg m⁻³

D_m not measured

Data collection

Bruker SMART CCD diffractometer

ω scans

Absorption correction:

multi-scan (SADABS; Sheldrick, 1996)

$T_{\min} = 0.957$, $T_{\max} = 0.996$

14 694 measured reflections

3496 independent reflections

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.044$

$wR(F^2) = 0.107$

$S = 1.035$

3496 reflections

255 parameters

All H-atom parameters refined

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 606 reflections

$\theta = 10.2$ – 20.8 °

$\mu = 0.140$ mm⁻¹

$T = 100$ (2) K

Plate

$0.32 \times 0.18 \times 0.03$ mm

Light yellow

2443 reflections with

$I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

$\theta_{\text{max}} = 29.96$ °

$h = -35 \rightarrow 34$

$k = -10 \rightarrow 10$

$l = -19 \rightarrow 19$

Intensity decay: none

$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.50P]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} < 0.001$

$\Delta\rho_{\text{max}} = 0.392$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.285$ e Å⁻³

Extinction correction: none

Scattering factors from

International Tables for

Crystallography (Vol. C)

N2S—H23S···O3 ^v	0.98 (2)	1.87 (2)	2.838 (2)	168 (2)
N3S—H31S···O2 ^{vi}	0.93 (2)	2.07 (2)	2.940 (2)	154 (2)
N3S—H32S···O4 ^{vii}	0.94 (2)	2.08 (2)	3.002 (2)	168 (2)
N4S—H41S···O3 ⁱ	0.97 (2)	1.85 (2)	2.808 (2)	169 (2)
N4S—H42S···N2 ⁱⁱ	0.95 (2)	2.08 (2)	3.027 (2)	170 (2)
N4S—H43S···O5 ^{viii}	0.97 (2)	1.81 (2)	2.763 (2)	167 (2)

Symmetry codes: (i) $x, y-1, z$; (ii) $-x, 2-y, -z$; (iii) $x-\frac{1}{2}, \frac{3}{2}-y, z-\frac{1}{2}$; (iv) $x-\frac{1}{2}, \frac{5}{2}-y, z-\frac{1}{2}$; (v) $-x, y, \frac{1}{2}-z$; (vi) $-x, y-1, \frac{1}{2}-z$; (vii) $x, 2-y, \frac{1}{2}+z$; (viii) $\frac{1}{2}-x, \frac{3}{2}-y, 1-z$.

All H atoms were located from difference Fourier maps and were refined isotropically without constraints.

Data collection: SMART (Bruker, 1998). Cell refinement: SMART. Data reduction: SAINT-Plus (Bruker, 1998). Program(s) used to solve structure: SHELX97 (Sheldrick, 1997). Program(s) used to refine structure: SHELX97. Molecular graphics: SHELX97. Software used to prepare material for publication: SHELX97.

Financial support from EPSRC is gratefully acknowledged.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1312). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1999). **C55**, 1536–1538

1-Hydroxy-2(1H)-pyridinethione

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(Received 2 February 1999; accepted 14 May 1999)

Abstract

1-Hydroxy-2(1H)-pyridinethione, C₅H₅NOS, crystallizes as the thione tautomer, with an intramolecular hydrogen bond between the hydroxyl and thione groups. C—H···O bonds link the molecules into centrosymmetric dimers which form a three-dimensional network via C—H···S interactions.

Table 1. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1—H10···O2 ⁱ	0.82 (2)	1.86 (2)	2.645 (2)	160 (2)
N3—H3N···N1S	0.83 (2)	2.11 (2)	2.928 (2)	168 (2)
N1S—H11S···O5 ⁱⁱ	0.89 (2)	2.17 (2)	2.996 (2)	154 (2)
N1S—H12S···O5 ⁱⁱⁱ	0.87 (2)	2.44 (2)	3.134 (2)	137 (2)
N2S—H21S···O4 ^{iv}	0.98 (2)	1.81 (2)	2.790 (2)	175 (2)
N2S—H22S···O6 ^v	0.99 (2)	1.99 (2)	2.831 (2)	141 (2)